

In Situ XAS Investigation of Vanadium Pentoxide Aerogel Cathodes

A.N. Mansour, P.H. Smith, W.M. Baker (Naval Surface Warfare Center), M. Balasubramanian and J. McBreen (BNL)

Beamline(s) X11A

Introduction: Nanophase vanadium pentoxide (V_2O_5) aerogel material synthesized using sol-gel techniques is being considered a potential alternative to the cobalt and nickel oxide systems as cathode materials for lithium (Li) batteries. The electrochemical performance of V_2O_5 , however, depends on its structure (i.e., crystalline vs. amorphous), morphology (i.e., particle size and surface area), and water content.

Methods and Materials: In Situ XAS combined with electrochemical charge and discharge methods was used to examine the evolution of the oxidation state and local structure of vanadium as a function of state of charge and cycling in a nonaqueous cell.

Results: We show that the oxidation state of V in V_2O_5 aerogel cathode heat treated in a vacuum oven at 220°C for 20.5 hours is similar to that of V in a commercially obtained sample of orthorhombic V_2O_5 . We also show that Li insertion during the first cycle of discharge leads to the reduction of V(V) to V(IV) and V(IV) to V(III) in a manner consistent with the stoichiometry of the sample, i.e., $Li_xV_2O_5$, (Figure 1). In addition, Li extraction during charge leads to oxidation of V(III) to V(IV) and then V(IV) to V(V). The oxidation state of V in fully charged cathodes is close to +5 and remains relatively unchanged with cycling (up to at least the 16th cycle). However, the average oxidation state of V in discharged V_2O_5 cathodes increases with cycling. We show that the local structure of V in the discharged state has a higher degree of symmetry than that of V in the fully charged state (Figure 2). Furthermore, a significant change in the structure of the V-V correlation of discharged cathodes is observed with cycling indicating the formation of electrochemically irreversible phases.

Conclusions: We have successfully illustrated variations in the oxidation state and local structure of V in V_2O_5 aerogel cathode as a function of states charge and discharge as well as cycling in a nonaqueous cell.

Acknowledgments: We gratefully acknowledge financial support by ONR, the Carderock Division of the Naval Surface Warfare Center's In-house Laboratory Independent Research Program administrated under ONR's Program Element 0601152N, and the US DOE (MB and JM).

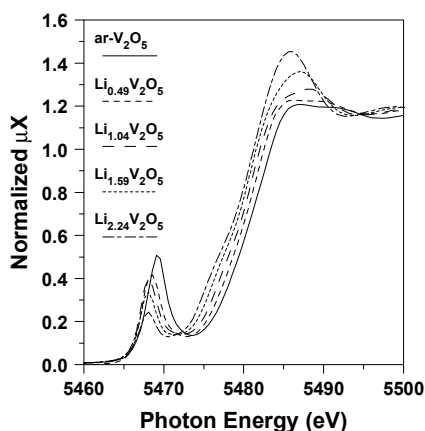


Figure 1. *In situ* V K-edge XANES for a V_2O_5 aerogel cathode as a function of states of discharge (i.e., lithium content or x in $Li_xV_2O_5$).

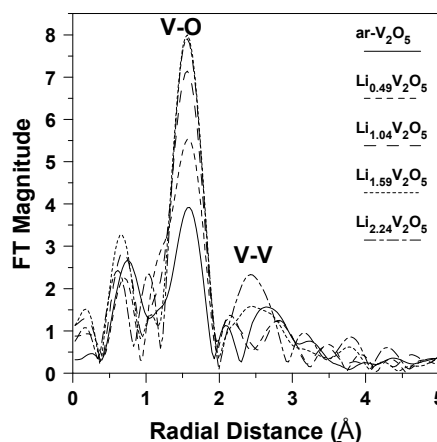


Figure 2. Fourier transform of K^3 -weighted V K-edge EXAFS spectra for a V_2O_5 aerogel cathode as a function of states of discharge (i.e., lithium content).